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(54) Title: METHOD OF PREPARING BLACK DYE FROM A NATURAL PRODUCT

(57) Abstract: The present invention relates to a method of preparing dye from natural materials. The dye derived from the method of the present invention may be used in the cosmetic, pharmaceutical and food industries.

METHOD OF PREPARING BLACK DYE FROM A NATURAL PRODUCT

Background of the Invention

Field of the Invention

The present invention relates to a method of preparing dye from natural materials. The dye derived from the method of the present invention can be used in the cosmetic, pharmaceutical and food industries.

Description of the Related Art

A method of preparing dye from the lobes, pistils and pollen of the hibiscus plant is well known. The method comprises extracting the dye using organic acids, removing the solvents, and drying and refining the dye into a form that can be sold commercially. The red dye prepared in this way is often used in cosmetics, such as lipstick, nail polish, shampoo and blush.

The disadvantages of using dye prepared from the hibiscus are that only red colors can be obtained and that the low adhesive properties of the dye prevent its use as a hair color product. In addition, the method of obtaining dye from the hibiscus is ecologically unsound because organic acids are used in the extraction.

Another known source of natural dyes is red algae. Red algae can be dried and ground, producing an insoluble powder made up of 200-400 micron particles. This dye has similar disadvantages to the dye obtained from hibiscus: it is only available in the color red and it can not be used as a hair color product because of its low adhesive properties.

A brown dye of natural origin can be prepared from the rind of a ripe walnut. Such a dye is described in USSR Certificate No. 1784623 (1992). This dye is often used in the food-processing industry to stain confectionery products brown so that they resemble chocolate. However, this dye tends to degrade over time. Thus, the dye cannot be used in foods, such as cookies, which require long-term storage. Additionally, the dye's lack of stability renders it unsuitable for cosmetics, such as hair color products. Moreover, the dye cannot be used for the coloring of foods such as artificial caviar because of poor adhesion. Furthermore, a black dye cannot be obtained from ripe walnut rinds, and brown dye is not suitable for forming artificial caviar.

A black dye used in food products is derived from drying and refining tea leaves. The tea leaves are ground to particles of 200-400 microns and water-extracted at 92°C for 20 minutes. The tea extract can be separated from the sediment by centrifugation and/or filtration. The extract is then dried and a soluble powder obtained. However, the low degree of extractability of this dye is disadvantageous.

Thus there exists a need for a black dye produced from natural materials that may be used in a wide variety of contexts, including hair color products, foodstuffs and cosmetics. There is an additional need for a method of producing such a dye in a high yield manner.

Summary of the Invention

The method of the present invention comprises obtaining unripe walnut rinds, drying said walnut rinds to produce dried walnut rinds, and grinding the dried walnut rinds to form a dispersible powder.

Detailed Description of the Preferred Embodiment

The method of the present invention includes drying and grinding the rind of unripe walnuts to form a dispersible powder. The drying is carried out until the water content of the rinds is no more than 20 weight %. The grinding is done in two stages: rasping grinding and ultradispersible grinding. In the rasping grinding, the material is crushed to a size of no more than 0.5-1 mm. In the following ultradispersible grinding, the product is simultaneously dried and ground in a rotational grinding mill in the presence of a gas stream at a temperature of no more than 80-90° C. The resulting particles have a size of less than 50 microns and have a water content of 2-3 weight %.

This dispersible powder may be used as a dye. In another embodiment, the dispersible powder is subject to water extraction for at least 30 minutes with boiling water. The ratio of the ultra-dispersible powder to water is no more than 1:7. The product may be settled or filtered to remove the sediment (the undissolved part of the material. A preservative such as academe benzoicum may be added to the liquid in an amount of 1.0-3.0 weight %. A vibration/acoustic field with a frequency of 10-100 Hz and with an oscillation frequency of 10-50 microns may be applied to

the mixture of ultradispersible powder/water during extraction of the product. The liquid extract is exposed to spray drying at a temperature of 100-170° C to produce the powder product having a water content of no more than 2-3 weight %.

The ability to extract dye from natural materials can be influenced by a number of different factors. In particular, the ability to extract dye depends upon the solubility of the dye in a particular solvent, such as water. It is well known that the solubility of dye contained in particles increases with the increasing surface area of the particles. Thus, reducing the dye-containing rind in the method of the present invention to dispersible particles of less than 100 microns increases the solubility and hence efficiency of extraction considerably compared to the use of 200-400 micron particles in methods known in the art.

Only six species of walnut are native to the United States. About fifteen others of this type of trees are from South America, the West Indies, Southern Europe and Asia. Any of these species can be used in the context of the present invention. The fruit of the walnut tree is a nut that grows on the tree. It is enclosed in a thick leathery shell which does not split open until it is ripe. The thick leathery shell is referred to herein as the "rind" of the walnut. Rinds which have not yet split open are referred to herein as "unripe" walnut rinds. The rind of unripe walnuts is used as a source material in the method of the present invention.

The rinds of unripe walnuts must be separated from the nutmeat and other components of the nut. This may be accomplished by any method known in the art, such as those techniques used for pitting prunes and other fruit. The rinds are dried until they contain no more than 50% water by weight. More preferably, the rinds are dried until they contain less than 20% water by weight. Any method of drying known in the art may be employed. One example is drying in a gas stream of 70-100°C.

The dried rind is then refined to produce a dispersible powder comprising particles less than 100 microns in diameter and containing no more than 10% water by weight. More preferably, the particles are no more than 50 microns in diameter and the dispersible powder contains no more than 2 to 3% water by weight. This may be done by any of a variety of methods known in the art. In the preferred embodiment, this is accomplished in two stages. In the first stage, the rinds are crushed to produce particles of no more than 0.1-10 mm in diameter.

More preferably, the particles produced are no more than 0.5-1 mm in diameter. In the second stage, the particles are further reduced in size to less than 100 microns in diameter. This may be done, for example, in a rotational grinding mill. Simultaneously the particles are further dried in a gas stream of no more 80-90 °C. The resulting dispersible powder is preferably composed of particles less than 100 microns in diameter and contains no more than 10% water by weight. More preferably, the particles of the resulting dispersible powder are no more than 50 microns in diameter and the dispersible powder contains no more than 2 to 3% water by weight. The dispersible powder may be used directly as a dye. For example it can be used to dye foodstuffs. Alternatively, the dispersible powder may be subject to water extraction as described below to produce a more pure dye.

The dispersible powder is mixed with water and extracted by boiling for not less than 30 minutes. The ratio of dispersible powder to water is preferably between 2:1 and 1:20. More preferably, the ratio of dispersible powder to water is no more than 1:7 during the water extraction. Following boiling, sediment is removed from the liquid extract. This may be done by any method known in the art. For example, the extract may be filtered.

In a further embodiment, during the extraction process the mixture of dispersible powder and water is subject to sonication. Preferably, the frequency will be not less than 10 Hz.

In one embodiment a preservative is added to the liquid extract to prevent breakdown of the dye. For example, benzoic acid (1-3% by weight) may be added to the liquid extract. In this embodiment, the liquid extract may be bottled and sold commercially as a dye that may be used, for example, in hair color products.

In another embodiment, the liquid extract is dried by spray drying at a temperature of 100-170°C. This will result in a powdered dye containing no more than 2-3% water by weight. However, any method known in the art for reducing a water-based extract to a powder may be used. The resulting powder may be sold commercially as a dye for use in cosmetics, foodstuffs and hair color products.

The black dye powder obtained by the method of the present invention contains natural biologically active compounds. For example, the dye may have anti-sclerotic activity and may reduce cholesterol when consumed in foodstuffs.

The rind of unripe (green) walnut is used to form black dye-stuff. The rind of the unripe walnut is separated from a pulp. The pulp may be used in making jams. In an alternative embodiment, the green (unripe) walnut may also be used to form the dyestuff.

EXAMPLE 1

An unripe (green) walnut or its oilcake with a humidity of 65-70 weight % is ground in a mill to a size of no more than 0.2 mm. The ground mass is pressed with a hydraulic press with a specific pressure of 25 tons to produce juice and oilcake. The oilcake is dried at a temperature of no higher than 300° C to achieve a residual moisture content of 3-5 weight %. The dried oilcake is ground in a vortical mill to form a powder with a particle size of 50-60 microns. The powder is mixed with walnut juice in a ratio of no more than 3.5:1, heated to a temperature of 100-120°C to form a gel. The gel is cooled to room temperature, mixed with ethyl alcohol in a ratio of not less than 10:1.

The mixture is maintained for not less than 60 minutes and filtered on an electromagnetic filter at a frequency of 2500 Hz with a vacuum pump. This method allows various impurities such as metal compounds, iodine, and other microelements to be removed from the dye-stuff. The filtered material is centrifuged at a speed of at least 5000 rpm for 30-60 minutes. The solid is heated to a temperature of no more than 150° C for 10-15 minutes, then thermally processed in a muffle furnace at a temperature of no more than 350° C for 5-10 minutes. The product is mixed with ethyl alcohol in a ratio of no more than 10:1, maintained for 20-30 minutes, and filtered. The solid product is collected and is ready for use as a black dye-stuff, for example, for dying artificial caviar. Before application, the black dye stuff is diluted with water by 5000 times. About 2 kg. of black dye-stuff concentrate is obtained from one ton of raw material.

EXAMPLE 2

Unripe walnuts together with their rinds or the rinds of unripe walnuts alone are placed in an 70-100°C airflow and dried until they contain no more than 20% water by weight. The rinds are then ground to produce medium-sized particles of 0.5-1 mm. These particles are further reduced in size in a rotational gas-dynamic grinder. The gas-dynamic grinder uses the energy of compressed air to crush the product particles in a vortex flow. The vortical mill was described in Pat. of

Russian Federation No. 2057588, Intern. Class 02 C, 19/06, published 10.04.96. The airflow is at a temperature of 80-95 °C, and the water content of the particles is reduced to 2-3% by weight. In this grinder the particles are reduced to less than 50 microns in diameter and take the form of a dispersible powder. The grinding occurs without appreciable heating or structural changes in the material. This powder may be packaged and sold commercially as, for example, a dye for confectionery articles in the food-processing industry.

EXAMPLE 3

The dispersible powder formed in EXAMPLE 2 is added to water at a ratio of no more than 1:7 powder to water. The mixture is then boiled for not less than 30 minutes. To facilitate the extraction of dye from the dispersible powder and to speed up the extraction time, the mixture may be subject to concurrent sonication at a frequency of not less than 10-100 Hz.

Any sediment is removed by filtration. Alternatively, the sediment may be allowed to settle and the liquid decanted. Benzoic acid may be added to the extract as a preservative in an amount of 1-3% by weight. At this point the extract may be bottled and sold commercially. One use of the extract is as a dye in hair color products.

EXAMPLE 4

The liquid extract obtained pursuant to EXAMPLE 3 prior to the addition of preservative is spray dried at a temperature of 100-170 °C. This results in a powder that is no more than 2-3% water by weight. This powder may be packaged and sold commercially for use as a dye in, for example, food products, cosmetics and hair color products.

EXAMPLE 5

The solubility of the dispersible powder produced according to the method of the present invention was measured and compared to the solubility of 100-200 micron particles of unripe walnut rind produced according to a traditional method described in the Russian Federation Patent No. 2035478. The solubility was evaluated based on the rate of extraction in boiling water. The results are presented in Table 1.

TABLE 1

Material	Rate of extraction (hours)	Solubility (%)
Dispersible powder prepared by the method of the present invention	0.5	77.0
100-200 micron particles manufactured according to traditional method	1.5	37.0

From Table 1 it is clear that the extraction of dye from the rind of unripe walnut rind according to the method of the present invention is more than 2 times greater than that prepared according to a traditional method. In addition, the rate of extraction is 3 times faster using the method of the present invention.

EXAMPLE 6

The black dye obtained by the method of the present invention may be used to color pharmaceutical drugs in capsules or food products, for example, artificial black calf. The dye-stuff from EXAMPLE 1, obtained from unripe (green) walnuts or its rind are dissolved in a ratio of 1:10 to form a liquid concentrate. The liquid concentrate is diluted in water in a ratio of 1:500. The dye stuff is cooled to a temperature below 15° C before coloring the calf pellets. The artificial calf pellets obtained in the granulating plant are colored with the extract for 5-10 minutes to form grey to black pellets. The dye stuff is washed away from the colored pellets with water followed by boiling water.

The dispersible powder from EXAMPLE 2 and the powdered dye from EXAMPLE 3 may also be used to color confectionery products, such as ice cream or cakes. The powder may be incorporated into the product during manufacture.

EXAMPLE 7

The liquid extract from EXAMPLE 3 and the powdered dye from EXAMPLE 3 may be used in hair color products. The liquid extract may be diluted in 100 times the volume of hot water. The powdered dye may be dissolved in hot water at the ratio of 5 g powdered dye per 500 ml of water. The resulting solution is applied to the hair for 20-40 minutes. The solution is then washed away with water.

In addition to color, the dye increases the luster of hair and does not cause the hair to become fragile. The dye does not cause dandruff.

WHAT IS CLAIMED IS:

1. A method of preparing a black dye, comprising:

obtaining unripe walnut rinds;

drying said walnut rinds to produce dried walnut rinds; and

grinding the dried walnut rinds to form a dispersible powder.

2. The method of Claim 1, wherein said dried walnut rinds contain no more than 20% water by weight.

3. The method of Claim 1, wherein said dried walnut rinds are further dried during said grinding.

4. The method of Claim 1, wherein said dispersible powder contains no more than 10% water by weight.

5. The method of Claim 1, wherein said grinding is accomplished in a plurality of steps.

6. The method of Claim 5, wherein a first grinding step produces particles of 0.1-10 mm in diameter.

7. The method of Claim 5, wherein a second grinding step produces particles of less than 100 microns in diameter.

8. The method of Claim 1, additionally comprising mixing said dispersible powder with water to form a mixture.

9. The method of Claim 8, wherein the mixture has a ratio of dispersible powder to water of from 2:1 to 1:20.

10. The method of Claim 8, additionally comprising boiling said mixture.

11. The method of Claim 8, additionally comprising sonicating said mixture.

12. The method of Claim 10, additionally comprising filtering the boiled mixture.

13. The method of Claim 12, additionally comprising drying the filtered mixture.

14. The method of Claim 12, additionally comprising adding a preservative to the filtered mixture.

15. The method of Claim 14, wherein said preservative is benzoic acid.

16. Application of the unripe (green) walnut or its rind as a material for preparation of black dye-stuff of natural origin.

17. A method of reception of black dye-stuff of natural origin, including crushing of material of vegetative origin and its drying.

18. The method of Claim 17, wherein the unripe (green) walnut or its rind as a vegetative material of natural origin is used.

19. The method of Claims 17 or 18, wherein the unripe walnut or its rind are ground to particles of no more than 0.2 mm.

20. The method of Claim 19, wherein the received mass is subject to pressing for manufacture of juice and oilcake.

21. The method of Claim 20, wherein the oilcake is dried to a residual water content of 3-5 weight%, the dried oilcake is ground in a vortical mill to receive the powder with particles of no more than 60 microns.

22. The method of Claim 21, wherein the resultant powder is mixed with the received walnut juice in the ratio of no more than 3, 5:1.

23. The method of Claim 21, wherein the mixture of powder with juice is heated and maintained at temperature of 100-120° to receive the gel mass.

24. The method of Claim 23, wherein the mixture is cooled at the room temperature, mixed with ethyl alcohol in the ratio of not less than 10:1.

25. The method of Claim 24, wherein the mixture is maintained within no less than 60 minutes and then filtered in an electric filter.

26. The method of Claim 25, wherein the mass is precipitated on the inner surfaces of the electric filter, collected and centrifuged at a rate of not less than 5000 rev/min within not less than 30 minutes.

27. The method of Claim 26, wherein the sediment from the centrifuge is previously heat-treated at temperatures of no more than 150° within 10-15 minutes.

28. The method of Claim 27, wherein the sediment is then thermal processed in a muffle furnace at a temperature of more than 350° within 5-10 minutes.

29. The method of Claim 28, wherein the received product is mixed with ethyl alcohol in the ratio of no more than 10:1, maintained within 20-30 minutes and filtered to receive the sediment on the filter inner surfaces.

30. The method of Claim 29, wherein the received sediment is the ready dye-stuff.

31. The method of Claim 30, wherein the ready dye-stuff is collected and packed in a tight packing.

32. A method according to Claims 17 or 18, wherein the drying is carried out until water content no more than 20 weight %.

33. A method according to Claims 17 or 18, wherein the refinement is realized in two stages: rasping, grinding and ultradisperse refinement.

34. A method according to Claims 17 or 18 wherein at the first stage of refinement the material is to be ground to the sizes of particles no more than 0, 5-1 mm.

35. A method according to Claims 18, 18, or 34, wherein the following repeated ultra-dispersible refinement is carried out simultaneously with additional drying in the vortical mill at the temperature of gas stream no more than 80-95°C.

36. A method according to Claim 35, wherein the powder of black dye-stuff is manufactured.

37. A method according to Claim 35, wherein after the additional drying in the vortical mill at the temperature of the gas stream of 80-95°C the particles of no more than 50 microns with their water content 2-3 weight% are received.

38. A method according to Claim 33, wherein the obtained ultra-dispersible powder of black-dye stuff is exposed to the extraction by water during not less than 30 minutes at the temperature of water boiling.

39. A method according to Claims 33 or 38, wherein the ratio of the ultra-dispersible powder of unripe walnut and water is no more than 1:7.

40. A method according to Claim 39, wherein the obtained product is settled or filtered with the following removing of the sediment (insoluble part of material).

41. A method according to Claims 38 or 39, wherein into the obtained liquid extract a preservative is entered.

42. A method according to Claim 41, wherein as a preservative may serve, for example, Acidum benzoicum in an amount 1.0-3.0 weight %.

43. A method according to any of Claims 38-42, wherein during the extraction of the product the admixture of the ultra-dispersible powder/water is exposed to the vibration-acoustic field with frequency no less than 10-100 Hz and oscillation frequency 10-50 microns.

44. A method according to Claim 43, wherein the obtained liquid extract of the black dye-stuff is exposed to the dissolving drying at the temperature of 100-100°C.

45. A method according to Claim 44, wherein the derived powder has a water content of no more than 2-3 weight %.